(19) Japan Patent Agency (JP)

(12) **Public Patent bulletin** (A)

(11) Public Patent Application Number

Tokkai 2001 – 172253

(P2001 – 172253A)

(43) Date of being Public Heisei 13, 26th June (2001. 6. 26)

(51) Int. Cl.[7]	Discrimination Number	
C 07 C 319/20		
B 01 J 31/02		103
C 07 C 323/12		
323/22		
323/65		
FI		Theme code (reference)
C 07 C 319/20		4H006
B 01 J 31/02	103X	4H039
C 07 C 323/12		
323/22		
323/65		

Investigation of Claims Nil

Number of Inventions 4

OL (Total 4 Pages(Japanese))

Continued on the last page

(21) Patent Application Number — Tokkai Hei 11 – 360589

(22) Date of Patent Application — Heisei 11 20th December (1999. 12. 20)

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(54) [Title of the invention]

Method for Manufacture of Sulfur-Containing Acrylic Compound.

(57) [Summary]

[Topic] (There exists correction)

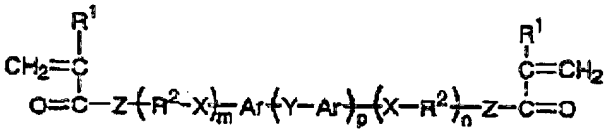
To offer a method to manufacture sulfur-containing acrylic compound that has satisfactory operability of hardening molding, is a liquid and that does not undergo crystallization at normal temperature.

[Method for solution]

To react sulfur-containing polyol with (metha) acrylic acid in the presence of esterification catalyst and solvent.

The sulfur-containing polyol is the compound shown by the general formula (1) given below.

[Formula 1]



(Wherein, R shows divalent hydrocarbon radical having 1 ~ 12 carbon atoms, X shows chlorine atom or bromine atom, Y shows – SO_2 -, - S - or – CO -, m and n are integers from 1 ~ 3 and p and q are integers from 0 ~ 4.)

[Scope of patent claims]

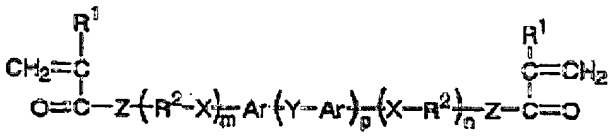
[Claim 1]

The method for manufacture of sulfur-containing acrylic compound has the characteristic of reacting sulfur containing-polyol with (metha) acrylic acid in the presence of esterification catalyst and solvent.

[Claim 2]

The method for manufacture of sulfur-containing acrylic compound described above in claim number 1 in which the sulfur containing-polyol is the compound shown by the general formula (1) given below.

[Formula 1]



(Wherein, R shows divalent hydrocarbon radical having 1 ~ 12 carbon atoms, X shows chlorine atom or bromine atom, Y shows – SO_2 -, - S - or – CO -, m and n are integers from 1 ~ 3 and p and q are integers from 0 ~ 4.)

[Claim 3]

The method for manufacture of sulfur-containing acrylic compound described above in claim number 1 or 2 in which the compound shown by the general formula (1) is at least 1 type chosen from 4, 4' – bis (2 – hydroxy ethyl thio) di phenyl sulfone, 4, 4' – bis (2 – hydroxy ethyl thio) di phenyl ketone, 2, 4 – bis (2 – hydroxy ethyl thio) di phenyl ketone and 4, 4' – bis (2 – hydroxy ethyl thio) 3, 3', 5, 5' – tetra bromo di phenyl ketone.

[Detailed description of the invention]

[0001]

[Technical field of the invention]

The present invention relates to the method for manufacture of sulfur-containing acrylic compound. In further details, the present invention relates to reformation of manufacturing method of sulfur-containing acrylic compound by subjecting sulfur-containing polyol to acylation. The sulfur-containing acrylic compound obtained by the present invention does not undergo crystallization at normal temperature due to which it is suitable as raw material of resin having high refractive index that is used in optical lenses, prisms etc.

[0002]

[Techniques of the past]

The fact that polymer of sulfur-containing acrylic compound can form molded material having high refractive index is known and different compounds and their manufacturing methods have

been proposed. As regards the manufacturing method of general sulfur-containing acrylic compound, the method of reacting sulfur-containing polyol with acylation agent such as (metha) acrylic acid halide, (metha) acrylic acid ester or (metha) acrylic acid is known. However, the sulfur-containing acrylic compound known up till now is manufactured by using (metha) acrylic acid halide as acylation agent (Patent number Sho 61 – 72748 and Sho 62 – 195357).

[0003]

[Problems the invention solves]

However, the sulfur-containing acrylic compound manufactured by using (metha) acrylic acid halide as acylation agent is either solid at room temperature or even though it is liquid, it undergoes crystallization when stored due to which injection for hardening molding becomes difficult. Moreover, the sulfur-containing acrylic compound manufactured by using (metha) acrylic acid ester as acylation agent also has many problems. The present invention aims at offering a method to manufacture sulfur-containing acrylic compound that does not undergo crystallization at normal temperature.

[0004]

[Method to solve the problems]

The authors of the present invention carried out an earnest research in the view of situation mentioned above as a result of which they showed that the sulfur-containing acrylic compound manufactured by using (metha) acrylic acid as acylation agent, is liquid and does not undergo crystallization even when storing for long time. Based on this knowledge, the present invention was completed. Namely, the present invention offers the method for manufacture of sulfur-containing acrylic compound that has the characteristic of reacting sulfur-containing polyol with (metha) acrylic acid in the presence of esterification catalyst and solvent.

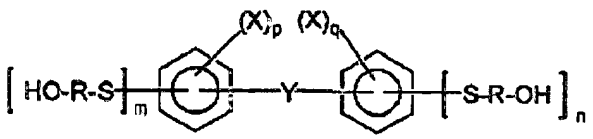
[0005]

[State of practicalization of the invention]

The present research has been explained below in further details. There is no particular restriction over the sulfur-containing polyol used in the present invention, however, the compound shown by the general formula (1) is desired.

[0006]

[Formula 2]



(1)

[0007]

(Wherein, R shows divalent hydrocarbon radical having 1 ~ 12 carbon atoms, X shows

chlorine atom or bromine atom, Y shows – SO_2 -, - S - or – CO -, m and n are integers from 1 ~ 3 and p and q are integers from 0 ~ 4.)

In formula (1), R shows divalent hydrocarbon radical having 1 ~ 12 carbon atoms and it can be straight chain, branched or cyclic. As regards the concrete examples, methylene radical, ethylene radical, tri methylene radical, propylene radical, tetra methylene radical etc. can be given. Among these, ethylene radical and propylene radical are desired.

[0008]

Moreover, as regards the concrete examples of this polyol compound, 4, 4' – bis (2 – hydroxy ethyl thio) di phenyl sulfone, 4, 4' – bis (2 – hydroxy ethyl thio) di phenyl ketone, 2, 4 – bis (2 – hydroxy ethyl thio) di phenyl ketone, 4, 4' – bis (2 – hydroxy ethyl thio) 3, 3', 5, 5' – tetra bromo di phenyl ketone can be given. Among these, 4, 4' – bis (2 – hydroxy ethyl thio) di phenyl sulfone and 4, 4' – bis (2 – hydroxy ethyl thio) di phenyl ketone are desired.

[0009]

Moreover, this polyol can be synthesized by the synthesis method described in N. Kharasch, volume 1, pages 97 ~ 111 or American patent 3,824,293. As regards the (metha) acrylic acid, marketed product can be used. Its usage quantity should be 2 ~ 10 mol, desirably 2 ~ 5 mol with respect to 1 mol of sulfur-containing polyol.

[0010]

Common esterification catalyst can be used as esterification catalyst. As regards the concrete examples, sulfuric acid, hydrochloric acid, phosphoric acid, boric acid fluoride, p – toluene sulfonic acid, benzene sulfonic acid, cation type ion exchange resin etc. can be given. Among these, p – toluene sulfonic acid and benzene sulfonic acid are desired. Its usage quantity should be within the range from 0.1 ~ 5 parts by weight with respect to 100 parts by weight of sulfur-containing polyol.

[0011]

As regards the polymerization preventing agent, hydroquinone, hydroquinone mono methyl ether, phenothiazine, copper salt etc. can be used. Its usage quantity should be 0.001 ~ 10 parts by weight, desirably 0.1 ~ 5 parts by weight with respect to 100 parts by weight of (metha) acrylic acid. In this esterification reaction, solvent is desired to be used as dehydrating agent also. As regards the solvent, benzene, toluene, xylene, tri chloro ethylene, tetra chloro ethylene etc. can be given. Among these also, benzene and toluene are particularly desired. Its usage quantity should be 50 ~ 500 parts by weight, desirably 100 ~ 300 parts by weight with respect to 100 parts by weight of sulfur-containing polyol.

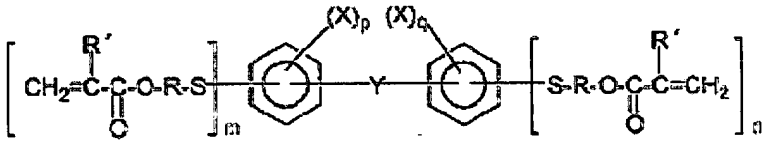
[0012]

The esterification reaction is carried out by taking sulfur-containing polyol, (metha) acrylic

acid, solvent, esterification catalyst and polymerization preventing agent in a reactor and carrying out heating under stirring under inert gas atmosphere desirably nitrogen simultaneously while removing the generated water out of the system by azeotropy. Reaction temperature should be within the range from 50 ~ 200^{0}C, desirably 80 ~ 150^{0}C, pressure is generally normal pressure and reaction time is within the range from 5 ~ 30 hours, desirably 8 ~ 20 hours. After the completion of esterification reaction, reaction solution is first washed with aqueous alkali solution such as caustic soda and then it is washed with water till it becomes neutral. Polymerization preventing agent is added to the reaction solution obtained after the completion of washing as per requirement and solvent is removed under reduced pressure when the aimed sulfur containing-acrylic compound is obtained. Moreover, in the case of sulfur-containing polyol being the compound shown by the general formula (1), sulfur-containing acrylic compound shown by the general formula (2) is obtained.

[0013]

[Formula 3]



(2)

[0014]

(Wherein, R' shows hydrogen atom or methyl radical, R shows divalent hydrocarbon radical having 1 ~ 12 carbon atoms, X shows chlorine atom or bromine atom, Y shows – SO_2 -, - S – or – CO -, m and n are integers from 1 ~ 3 and p and q are integers from 0 ~ 4.)

In formula (2), R shows divalent hydrocarbon radical having 1 ~ 12 carbon atoms and it can be straight chain, branched or cyclic. As regards the concrete examples, methylene radical, ethylene radical, tri methylene radical, propylene radical, tetra methylene radical etc. can be given. Among these, ethylene radical and propylene radical are desired.

[0015]

As regards the concrete examples of compound shown by the formula (2), 4, 4' – bis (β - methacryloyloxy ethyl thio) di phenyl sulfone, 4, 4' – bis (β - acryloyloxy ethyl thio) di phenyl sulfone, 4, 4' – bis (β - methacryloyloxy ethyl thio) di phenyl ketone, 4, 4' – bis (β - acryloyloxy ethyl thio) di phenyl ketone, 2, 4 – bis (β - methacryloyloxy ethyl thio) di phenyl ketone, 2, 4 – bis (β - acryloyloxy ethyl thio) di phenyl ketone, 4, 4' – bis (β - methacryloyloxy ethyl thio) 3, 3', 5, 5' – tetra bromo di phenyl ketone etc. can be given.

[0016]

[Practical examples]

The present invention has been explained below in further details with the help of practical examples and comparative examples. However, the present invention is not restricted only to these practical examples.

Practical example 1

200 parts by weight of 4, 4' – bis (2 – hydroxy ethyl thio) di phenyl sulfone, 130 parts by weight of methacrylic acid, 0.27 parts by weight of hydroquinone mono methyl ether, 0.80 parts by weight of copper powder, 5 parts by weight of p – toluene sulfonic acid and 270 parts by weight of toluene were taken in a 1-liter flask having 4 openings equipped with a stirrer, thermometer, condenser, water separator and 4 cc air was flown in the reaction system per minute and reaction was carried out at 90 ~ 130^{0}C for 6 hours simultaneously while extracting the generated water. After the completion of reaction, it was cooled up to normal temperature and 270 parts by weight of toluene was added after which it was washed with 5 % aqueous solution of sodium hydroxide and then with water till it becomes neutral. After that, 0.27 parts by weight of hydroquinone mono methyl ether was added and toluene was removed at 60^{0}C under reduced pressure of 5 Torr for 2 hours when 260 parts by weight of 4, 4' – bis (β - methacryloyloxy ethyl thio) di phenyl sulfone was obtained. The obtained 4, 4' – bis (β - methacryloyloxy ethyl thio) di phenyl sulfone was liquid at normal temperature.

[0017]

Practical example 2

115 parts by weight of acrylic acid was used instead of methacrylic acid. Other than this change, reaction similar practical example 1 was carried out when 250 parts by weight of 4, 4' – bis (β - acryloyloxy ethyl thio) di phenyl sulfone was obtained. The obtained 4, 4' – bis (β - acryloyloxy ethyl thio) di phenyl sulfone was liquid at normal temperature.

[0018]

Comparative example 1

100 parts by weight of 4, 4' – bis (2 – hydroxy ethyl thio) di phenyl sulfone and 200 parts by weight of methyl ethyl ketone were taken in a 1-liter flask having 4 openings equipped with a stirrer, thermometer, condenser, water separator and it was dissolved by heating and stirring at 60^{0}C under nitrogen gas atmosphere after which 60 parts by weight of pyridine was added and solution was cooled to 0 ~ 5^{0}C simultaneously while stirring and 70 parts by weight of methacrylic acid chloride was dropped for 1 hours simultaneously while maintaining this temperature. Next, it was heated at 40^{0}C for 2 hours after which reaction liquid was poured in water and extracted by s500 parts by weight of toluene. After this, procedure similar to practical example 1 was carried out when 260 parts by weight of 4, 4' – bis (β - methacryloyloxy ethyl thio) di phenyl sulfone was

obtained. The obtained 4, 4' – bis (β - methacryloyloxy ethyl thio) di phenyl sulfone was liquid at the time of manufacturing, however, it underwent crystallization after 1 week and became solid.

[0019]

Comparative example 2

(Reaction by transesterification)

100 parts by weight of 4, 4' – bis (2 – hydroxy ethyl thio) di phenyl sulfone, 300 parts by weight of methyl methacrylate, 0.15 parts by weight of hydroquinone mono methyl ether and 200 parts by weight of toluene were taken in a 1-liter flask having 4 openings equipped with a stirrer, thermometer, condenser, water separator and when temperature was increased to 80^0C simultaneously while stirring, 2.7 parts by weight of tetra butyl titanate was added. After that, temperature was further increased and reaction was carried out at 100 ~120^0C for 15 hours simultaneously while removing methanol. After reaction, excess methyl methacrylate was removed and reaction solution was then cooled to room temperature. 200 parts by weight of toluene was added to this solution and after this, procedure similar to practical example 1 was carried out when 260 parts by weight of 4, 4' – bis (β - methacryloyloxy ethyl thio) di phenyl sulfone was obtained. The obtained 4, 4' – bis (β - methacryloyloxy ethyl thio) di phenyl sulfone was liquid at the time of manufacturing, however, it underwent crystallization after 1 week and became solid.

[0020]

[Effect / result of the invention]

Sulfur-containing acrylic compound that is liquid and does not undergo crystallization and has satisfactory operability of hardening molding can be manufactured by the method of the present invention.

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(51) Int. Cl.[7] Discrimination

Number

// C 07 B 61/00 300

FI Theme code (reference)

C 07 B 61/00 300

F Theme (Reference)

4H006 AA02 AC48 BA35 BA36 BA66
BA72 BB11 BB12 TA02 TA04
TB04
4H039 CA66 CD10 CD30